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Solvophobic Acceleration of a Diels–Alder Reaction in True Solutions in Organic Solvents

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Abstract

© 2018 Wiley Periodicals, Inc. The rate of Diels–Alder reaction of diene 9,10-bis(hydroxymethyl)anthracene with dienophile N-ethylmaleimide was studied in a series of solvents with different polarity and hydrogen-bonding ability. Enthalpies and entropies of activation were determined from the temperature dependences of the rate constants. Rate acceleration in nonaqueous protic solvents such as glycerol, propylene, and ethylene glycols was observed. In addition, enthalpy versus entropy of activation plots show a compensation pattern different from the other considered solvents, which can be linked with the solvophobic effects observed in polyhydric alcohols. However, the solvophobic acceleration was not as strong as the hydrophobic acceleration in water. Hydrogen bonding of the reactants and transition state with solvent also influences the reaction rate. The studied reaction is slightly promoted in hydrocarbon solvents in comparison with aprotic polar solvents. This was explained by hydrogen bonding of the hydroxyl groups of diene with dienophile in transition state, which requires prior breaking of the hydrogen bonds of these groups with polar solvent molecules.

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